

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 May 2006 (11.05.2006)

PCT

(10) International Publication Number
WO 2006/049863 A1

(51) International Patent Classification:
C08K 3/22 (2006.01) C08K 7/08 (2006.01)

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(21) International Application Number:
PCT/US2005/037410

(22) International Filing Date: 17 October 2005 (17.10.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/978,286 29 October 2004 (29.10.2004) US

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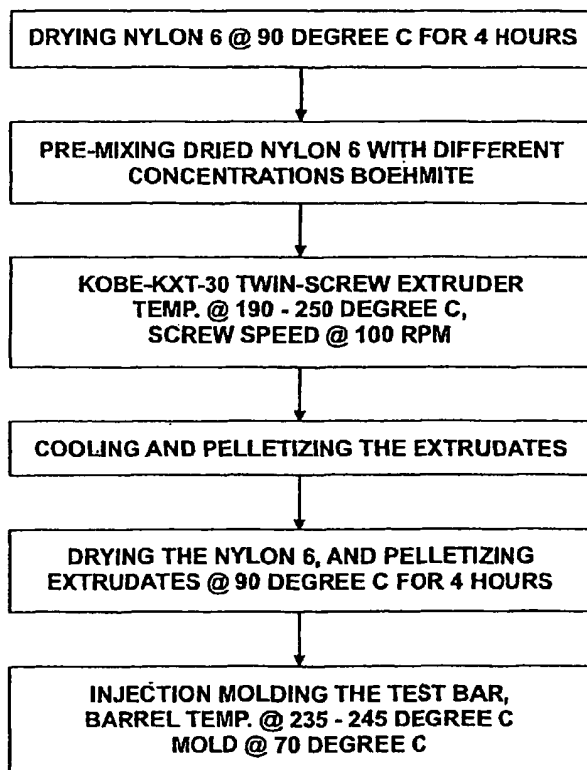
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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY,
MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK,
SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,

[Continued on next page]

(54) Title: FLAME RETARDANT COMPOSITES



(57) Abstract: A flame retardant polymer compos-
ite is disclosed. The composite includes a polymer
base material and a flame retardant filler provided in
the polymer base material, the flame retardant filler
containing seeded boehmite particulate material hav-
ing an aspect ratio of not less than 3:1.

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RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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FLAME RETARDANT COMPOSITES

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CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application is (i) a continuation-in-part application of US Patent Application 10/414,590, filed April 16, 2003, which in turn is a non-provisional application of US Provisional Application 60/374,014 filed April 19, 2002, and (ii) a continuation-in-part application of US Patent Application 10/823,400, filed April 13, 2004, and (iii) a continuation-in-part of US Patent Application 10/845,764, filed May 14, 2004. Priority to the foregoing applications is hereby claimed, and the subject matter thereof hereby incorporated by reference.

BACKGROUND

Field of the Invention

[0002] The present invention is generally directed to flame retardant composites, and more particularly to flame retardant composites that include a polymer base material and a flame retardant filler to improve flame retardancy.

Description of the Related Art

[0003] With rapid improvement in technology over the past decades, increasing demand has been created for high performance materials, including ceramics, metals and polymers for a myriad of applications. For example, in the context of microelectronic devices, market pressures dictate smaller, faster and more sophisticated end products, which occupy less volume and operate at higher current densities. These higher current densities further increase heat generation and, often, operating temperatures. In this context, it has become increasingly important for safety concerns to implement microelectronic packaging materials that provide

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exemplary flame resistance. Use of flame resistant packaging materials is but one example among many in which product designers have specified use of flame resistant materials. For example, flame resistant thermoplastic polymers are in demand as construction materials.

[0004] In addition, governmental regulatory bodies have also sought flame resistant materials in certain applications to meet ever-increasing safety concerns. Accordingly, the industry has continued to demand improved composite materials, for example, improved polymer-based materials that have desirable flame retardant characteristics.

SUMMARY

[0005] According to an aspect of the present invention, a flame retardant polymer composite is provided. The composite includes a polymer base material and a flame retardant filler provided in the polymer base material, the flame retardant filler containing seeded boehmite particulate material having an aspect ratio of not less than 2:1, typically not less than 3:1.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The present invention may be better understood, and its numerous objects, features, and advantages made apparent to those skilled in the art by referencing the accompanying drawings.

[0007] FIG. 1 illustrates a process flow for forming a polymer composite according to an embodiment of the present invention.

[0008] FIG. 2 illustrates a thermogravimetric analysis (TGA) of seeded boehmite vs. conventional ATH.

[0009] The use of the same reference symbols in different drawings indicates similar or identical items.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0010] According to one aspect of the present invention, a flame retardant polymer composite is provided, which includes a polymer base material and a flame retardant filler. Notably the flame retardant filler includes a seeded boehmite particulate material having an aspect ratio of not less than about 3:1. Typically, the polymer based material is a material that has commercial significance and demand in industry, but oftentimes does not exhibit native flame retardant properties. Quantitatively, flame retardancy may be measured according to underwriter laboratories test UL 94, the so called vertical burn test. The UL 94 test is carried out by ASTM D635 standards, and materials are given a V rating based upon several observed characteristics including flame time, glow time, extent of burning, as well as the ability of the sample to ignite cotton. Typically, the polymer based materials of interest and in need of flame retardant characteristics have a UL 94 rating of V-2 or above, indicating volatility under certain conditions. Additional features of the polymer base material according to embodiments of the present invention are discussed below. First, we turn to the flame retardant filler, particularly, the seeded boehmite particulate material according to embodiments of the present invention that contributes to significant improvement in flame retardancy.

[0011] According to a particular feature, the seeded boehmite particulate material is utilized rather than boehmite derived from non-seeded processing pathways, including non-seeded hydrothermal treatment and precipitation pathways. As discussed in more detail below, embodiments of the present invention have demonstrated exemplary flame retardancy, even without relying on additional flame retardant components to improve performance.

[0012] Seeded boehmite particulate material is generally formed by a process that includes providing a boehmite precursor and boehmite seeds in a suspension, and heat treating (such as by hydrothermal treatment) the suspension (alternatively sol or slurry) to convert the boehmite precursor into boehmite particulate material formed of particles or crystallites. According to a particular aspect, the boehmite particulate material has a relatively elongated morphology, described generally herein in terms of aspect ratio, described below.

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[0013] The term "boehmite" is generally used herein to denote alumina hydrates including mineral boehmite, typically being $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and having a water content on the order of 15%, as well as psuedoboehmite, having a water content higher than 15%, such as 20-38% by weight. It is noted that boehmite (including psuedoboehmite) has a particular and identifiable crystal structure, and accordingly unique X-ray diffraction pattern, and as such, is distinguished from other aluminous materials including other hydrated aluminas such as ATH (aluminum trihydroxide) a common precursor material used herein for the fabrication of boehmite particulate materials.

[0014] The aspect ratio, defined as the ratio of the longest dimension to the next longest dimension perpendicular to the longest dimension, is generally not less than 2:1, and preferably not less than 3:1, 4:1, or 6:1. Indeed, certain embodiments have relatively elongated particles, such as not less than 9:1, 10:1, and in some cases, not less than 14:1. With particular reference to needle-shaped particles, the particles may be further characterized with reference to a secondary aspect ratio defined as the ratio of the second longest dimension to the third longest dimension. The secondary aspect ratio is generally not greater than 3:1, typically not greater than 2:1, or even 1.5:1, and oftentimes about 1:1. The secondary aspect ratio generally describes the cross-sectional geometry of the particles in a plane perpendicular to the longest dimension.

[0015] Platey or platelet-shaped particles generally have an elongated structure having the aspect ratios described above in connection with the needle-shaped particles. However, platelet-shaped particles generally have opposite major surfaces, the opposite major surfaces being generally planar and generally parallel to each other. In addition, the platelet-shaped particles may be characterized as having a secondary aspect ratio greater than that of needle-shaped particles, generally not less than about 3:1, such as not less than about 6:1, or even not less than 10:1. Typically, the shortest dimension or edge dimension, perpendicular to the opposite major surfaces or faces, is generally less than 50 nanometers.

[0016] Morphology of the seeded boehmite particulate material may be further defined in terms of particle size, more particularly, average particle size. Here, the seeded boehmite particulate material, that is, boehmite formed through a seeding process (described in more detail below) has a relatively fine particle or crystallite

size. Generally, the average particle size is not greater than about 1000 nanometers, and fall within a range of about 100 to 1000 nanometers. Other embodiments have even finer average particle sizes, such as not greater than about 800 nanometers, 600 nanometers, 500 nanometers, 400 nanometers, and even particles having an average particle size smaller than 300 nanometers, representing a fine particulate material. In certain embodiments, the average particle size was less than 200 nanometers, such as within a range of about 100 nanometers to about 150 nanometers.

[0017] As used herein, the “average particle size” is used to denote the average longest or length dimension of the particles. Due to the elongated morphology of the particles, conventional characterization technology is generally inadequate to measure average particle size, since characterization technology is generally based upon an assumption that the particles are spherical or near-spherical. Accordingly, average particle size was determined by taking multiple representative samples and physically measuring the particle sizes found in representative samples. Such samples may be taken by various characterization techniques, such as by scanning electron microscopy (SEM).

[0018] The present seeded boehmite particulate material has been found to have a fine average particle size, while oftentimes competing non-seeded based technologies are generally incapable of providing such fine average particle sizes in the context of anisotropic particles. In this regard, it is noted that oftentimes in the literature, reported particle sizes are not set forth in the context of averages as in the present specification, but rather, in the context of nominal range of particle sizes derived from physical inspection of samples of the particulate material. Accordingly, the average particle size will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle size distribution. Stated alternatively, while non-seeded based technologies may report fine particle size, such fine sizing generally denotes the lower limit of an observed particle size distribution and not average particle size.

[0019] Likewise, in a similar manner, the above-reported aspect ratios generally correspond to the average aspect ratio taken from representative sampling, rather than upper or lower limits associated with the aspect ratios of the particulate material. Oftentimes in the literature, reported particle aspect ratios are not set forth in the

context of averages as in the present specification, but rather, in the context of nominal range of aspect ratios derived from physical inspection of samples of the particulate material. Accordingly, the average aspect ratio will lie within the reported range in the prior art, generally at about the arithmetic midpoint of the reported range, for the expected Gaussian particle morphology distribution. Stated alternatively, while non-seeded based technologies may report aspect ratio, such data generally denotes the lower limit of an observed aspect ratio distribution and not average aspect ratio.

[0020] In addition to aspect ratio and average particle size of the particulate material, morphology of the particulate material may be further characterized in terms of specific surface area. Here, the commonly available BET technique was utilized to measure specific surface area of the particulate material. According to embodiments herein, the boehmite particulate material has a relatively high specific surface area, generally not less than about $10 \text{ m}^2/\text{g}$, such as not less than about $50 \text{ m}^2/\text{g}$, $70 \text{ m}^2/\text{g}$, or not less than about $90 \text{ m}^2/\text{g}$. Since specific surface area is a function of particle morphology as well as particle size, generally the specific surface area of embodiments was less than about $400 \text{ m}^2/\text{g}$, such as less than about 350 or $300 \text{ m}^2/\text{g}$.

[0021] Turning to the details of the processes by which the boehmite particulate material may be manufactured, generally ellipsoid, needle, or platelet-shaped boehmite particles are formed from a boehmite precursor, typically an aluminous material including bauxitic minerals, by hydrothermal treatment as generally described in the commonly owned patent described above, US Patent 4,797,139. More specifically, the boehmite particulate material may be formed by combining the boehmite precursor and boehmite seeds in suspension, exposing the suspension (alternatively sol or slurry) to heat treatment to cause conversion of the raw material into boehmite particulate material, further influenced by the boehmite seeds provided in suspension. Heating is generally carried out in an autogenous environment, that is, in an autoclave, such that an elevated pressure is generated during processing. The pH of the suspension is generally selected from a value of less than 7 or greater than 8, and the boehmite seed material has a particle size finer than about 0.5 microns. Generally, the seed particles are present in an amount greater than about 1% by weight of the boehmite precursor (calculated as Al_2O_3), and heating is carried out at a

temperature greater than about 120°C, such as greater than about 125°C, or even greater than about 130°C, and at a pressure greater than about 85 psi, such as greater than about 90 psi, 100 psi, or even greater than about 110 psi.

[0022] The particulate material may be fabricated with extended hydrothermal conditions combined with relatively low seeding levels and acidic pH, resulting in preferential growth of boehmite along one axis or two axes. Longer hydrothermal treatment may be used to produce even longer and higher aspect ratio of the boehmite particles and/or larger particles in general.

[0023] Following heat treatment, such as by hydrothermal treatment, and boehmite conversion, the liquid content is generally removed, such as through an ultrafiltration process or by heat treatment to evaporate the remaining liquid. Thereafter, the resulting mass is generally crushed, such to 100 mesh. It is noted that the particulate size described herein generally describes the single crystallites formed through processing, rather than the aggregates which may remain in certain embodiments (e.g., for those products that call for and aggregated material).

[0024] According to data gathered by the present inventors, several variables may be modified during the processing of the boehmite raw material, to effect the desired morphology. These variables notably include the weight ratio, that is, the ratio of boehmite precursor to boehmite seed, the particular type or species of acid or base used during processing (as well as the relative pH level), and the temperature (which is directly proportional to pressure in an autogenous hydrothermal environment) of the system.

[0025] In particular, when the weight ratio is modified while holding the other variables constant, the shape and size of the particles forming the boehmite particulate material are modified. For example, when processing is carried at 180°C for two hours in a 2 weight % nitric acid solution, a 90:10 ATH:boehmite seed ratio forms needle-shaped particles (ATH being a species of boehmite precursor). In contrast, when the ATH:boehmite seed ratio is reduced to a value of 80:20, the particles become more elliptically shaped. Still further, when the ratio is further reduced to 60:40, the particles become near-spherical. Accordingly, most typically the ratio of boehmite precursor to boehmite seeds is not less than about 60:40, such as not less

than about 70:30 or 80:20. However, to ensure adequate seeding levels to promote the fine particulate morphology that is desired, the weight ratio of boehmite precursor to boehmite seeds is generally not greater than about 99:1, or 98:2. Based on the foregoing, an increase in weight ratio generally increases aspect ratio, while a decrease in weight ratio generally decreased aspect ratio.

[0026] Further, when the type of acid or base is modified, holding the other variables constant, the shape (e.g., aspect ratio) and size of the particles are affected. For example, when processing is carried out at 100°C for two hours with an ATH:boehmite seed ratio of 90:10 in a 2 weight % nitric acid solution, the synthesized particles are generally needle-shaped, in contrast, when the acid is substituted with HCl at a content of 1 weight % or less, the synthesized particles are generally near spherical. When 2 weight % or higher of HCl is utilized, the synthesized particles become generally needle-shaped. At 1 weight % formic acid, the synthesized particles are platelet-shaped. Further, with use of a basic solution, such as 1 weight % KOH, the synthesized particles are platelet-shaped. If a mixture of acids and bases is utilized, such as 1 weight % KOH and 0.7 weight % nitric acid, the morphology of the synthesized particles is platelet-shaped.

[0027] Suitable acids and bases include mineral acids such as nitric acid, organic acids such as formic acid, halogen acids such as hydrochloric acid, and acidic salts such as aluminum nitrate and magnesium sulfate. Effective bases include, for example, amines including ammonia, alkali hydroxides such as potassium hydroxide, alkaline hydroxides such as calcium hydroxide, and basic salts.

[0028] Still further, when temperature is modified while holding other variables constant, typically changes are manifested in particle size. For example, when processing is carried out at an ATH:boehmite seed ratio of 90:10 in a 2 weight % nitric acid solution at 150°C for two hours, the crystalline size from XRD (x-ray diffraction characterization) was found to be 115 Angstroms. However, at 160°C the average particle size was found to be 143 Angstroms. Accordingly, as temperature is increased, particle size is also increased, representing a directly proportional relationship between particle size and temperature.

[0029] The following examples focus on seeded boehmite synthesis.

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[0030] Example 1, Plate-shaped particle synthesis

[0031] An autoclave was charged with 7.42 lb. of Hydral 710 aluminum trihydroxide purchased from Alcoa; 0.82 lb of boehmite obtained from SASOL under the name-- Catapal B pseudoboehmite; 66.5 lb of deionized water; 0.037 lb potassium hydroxide; and 0.18 lb of 22wt% nitric acid. The boehmite was pre-dispersed in 5 lb of the water and 0.18 lb of the acid before adding to the aluminum trihydroxide and the remaining water and potassium hydroxide.

[0032] The autoclave was heated to 185°C. over a 45 minute period and maintained at that temperature for 2 hours with stirring at 530 rpm. An autogenously generated pressure of about 163 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 10. The liquid content was removed at a temperature of 65°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 62 m²/g. Average particle size (length) was within a range of about 150 to 200 nm according to SEM image analysis.

[0033] Example 2, Needle-shaped particle synthesis

[0034] An autoclave was charged with 250 g of Hydral 710 aluminum trihydroxide purchased from Alcoa; 25 g of boehmite obtained from SASOL under the name-- Catapal B pseudoboehmite; 1000 g of deionized water; and 34.7 g of 18% nitric acid. The boehmite was pre-dispersed in 100 g of the water and 6.9 g of the acid before adding to the aluminum trihydroxide and the remaining water and acid.

[0035] The autoclave was heated to 180°C. over a 45 minute period and maintained at that temperature for 2 hours with stirring at 530 rpm. An autogenously generated pressure of about 150 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 3. The liquid content was removed at a temperature of 95°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 120 m²/g. Average particle size (length) was within a range of about 150 to 200 nm according to SEM image analysis.

[0036] Example 3, Ellipsoid shaped particle synthesis

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[0037] An autoclave was charged with 220 g of Hydral 710 aluminum trihydroxide purchased from Alcoa; 55 g of boehmite obtained from SASOL under the name-- Catapal B pseudoboehmite; 1000 g of deionized water; and 21.4 g of 18% nitric acid. The boehmite was pre-dispersed in 100 g of the water and 15.3 g of the acid before adding to the aluminum trihydroxide and the remaining water and acid.

[0038] The autoclave was heated to 172°C. over a 45 minute period and maintained at that temperature for 3 hours with stirring at 530 rpm. An autogenously generated pressure of about 120 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 4. The liquid content was removed at a temperature of 95°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 135 m²/g. Average particle size (length) was within a range of about 150 to 200 nm according to SEM image analysis

[0039] Example 4, Near Spherical Particle synthesis

[0040] An autoclave was charged with 165 g of Hydral 710 aluminum trihydroxide purchased from Alcoa; 110 g of boehmite obtained from SASOL under the name-- Catapal B pseudoboehmite; 1000 g of deionized water; and 35.2 g of 18% nitric acid. The boehmite was pre-dispersed in 100 g of the water and 30.6 g of the acid before adding to the aluminum trihydroxide and the remaining water and acid.

[0041] The autoclave was heated to 160°C. over a 45 minute period and maintained at that temperature for 2.5 hours with stirring at 530 rpm. An autogenously generated pressure of about 100 psi was reached and maintained. Thereafter the boehmite dispersion was removed from the autoclave. After autoclave the pH of the sol was about 3.5. The liquid content was removed at a temperature of 95°C. The resultant mass was crushed to less than 100 mesh. The SSA of the resultant powder was about 196 m²/g.

[0042] Turning to the polymer base material of the composite, the material may be formed of polymers including elastomeric materials, such as polyolefins, polyesters, fluoropolymers, polyamides, polyimides, polycarbonates, polymers containing styrene, epoxy resins, polyurethane, polyphenol, silicone, or combinations thereof. In

one exemplary embodiment, the polymer composite is formed of silicone, silicone elastomer, and silicone gels. Silicone, silicone elastomer, and silicone gels may be formed using various organosiloxane monomers having functional groups such as alkyl groups, phenyl groups, vinyl groups, glycidoxy groups, and methacryloxy groups and catalyzed using platinum-based or peroxide catalyst. Exemplary silicones may include vinylpolydimethylsiloxane, polyethyltriepoxysilane, dimethyl hydrogen siloxane, or combinations thereof. Further examples include aliphatic, aromatic, ester, ether, and epoxy substituted siloxanes. In one particular embodiment, the polymer composite comprises vinylpolydimethylsiloxane. In another particular embodiment, the polymer composite comprises dimethyl hydrogen siloxane. Silicone gels are of particular interest for tackiness and may be formed with addition of a diluent.

[0043] Aspects of the present invention are particularly useful for polymer base materials that do not have a native, robust flame retardancy, such as those polymers that have a flame retardancy of V-2 or greater. For example, Nylon 6, noted below, has been characterized as having a native flame retardancy of V-2. Accordingly, as a subset of polymers that benefit from flame retardancy additives according to aspects of the present invention include: non-chlorinated polymers, non-fluorinated polymers, and may be selected from the group consisting of polyolefins, polyesters, polyamides, polyimides, polycarbonates, polymers containing styrene, epoxy resins, polyurethane, polyphenol, and combinations thereof.

[0044] The polymer composite may comprise at least about 0.5 to about 50 wt% boehmite particulate material, such as about 2 to about 30 wt%. According to one feature, exemplary flame retardancy may be achieved even a low loadings, such as within a range of about 2 to 15 wt% of the total composite.

[0045] Oftentimes the composite material is in the form of a component (cured form), and may find practical use as a polymer structural component such as a construction material. Typically, the polymer base material is combined with the boehmite filler material to form the composite, such as by mixing the components and, in the case of structural components, followed shape forming. Shape forming would not be required in the case of coating compositions.

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[0046] Turning to FIG. 1, a process for forming a polymer component in which a polymer base component is combined with boehmite. In the particular process flow, a molded polymer component is formed by injection molding. FIG. 1 details the process flow for nylon 6-based polymer component that may take on various contours and geometric configurations for the particular end use. As described, nylon-6 raw material is first dried, followed by premixing with boehmite under various loading levels. The premixed nylon-boehmite is then extruded to form pelletized extrudates, which are then cooled and dried. The final article is then formed by injection molding, the pelletized extrudates providing the feedstock material for the molding process. The particular geometric configuration may vary widely depending upon the end use, but here, flat bars were extruded that were then used as test samples for flame retardancy.

[0047] Following the foregoing process flow, two different filler loading levels were selected for flame retardancy testing, 3 wt.% and 5 wt.% of needle shaped (alternatively referred to as whisker or rod-shaped) fine boehmite. The samples were tested according to UL 94V, utilizing the classifying criteria below in Table 1.

[0048] Table 1

| Criteria Conditions | 94V-0 | 94V-1 | 94V-2 |
|---|-------|-------|-------|
| Flame time, T1 or T2 | ≤10s | ≤30s | ≤30s |
| Flame Time, T1 + T2 | ≤50s | ≤250s | ≤250s |
| Glow Time, T3 | ≤30s | ≤60s | ≤60s |
| Did sample burn to holding clamp? yes/no | No | No | No |
| Did sample ignite cotton? Yes/no | No | No | Yes |

[0049] As a result of testing, both the 3 wt.% and 5 wt.% loading levels provided the highly desirable V-0 rating. Such exemplary flame retardancy is notable, for various reasons. For example, the V-0 rating was achieved at very moderate loading levels, and without inclusion of additional flame retardant fillers. It should be noted, however, that additional fillers may be incorporated in certain embodiments to achieve additional flame retardancy, although the particular seeded boehmite material described above provides a marked improvement in flame retardancy without relying upon additional fillers.

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[0050] The above-reported flame retardancy takes on even additional significance when compared to the state of the art. For example, other reports have been provided in which fine boehmite material has only been able to provide limited flame retardancy, and not V-0 as reported herein. However, the boehmite additives utilized in these other reports is generally not a seeded boehmite, and is formed through a non-seeded process, including non-seeded hydrothermal processing pathways, or by precipitation. While not wishing to be bound by any particular theory, it is believed that the seeded processing pathway contributes to the exemplary flame retardancy reported herein. One possible explanation for this is that the seeded boehmite material has unique morphological features, perhaps even beyond the morphologies described above in connection with primary and secondary aspect ratios forming elongated platelet and needle-shaped particulates. However, it is additionally believed that the high aspect ratio morphologies enabled by seeded processing pathway may also further contribute to the exemplary flame retardancy. The high aspect ratio particles may provide a serpentine or tortuous pathway for oxygen migration, thereby inhibiting flame propagation due to reduced oxygen migration to the flame front or area.

[0051] Turning to FIG. 2, the results of thermogravimetric analysis (TGA) are reported for whisker (needle) shaped boehmite, as compared to conventional ATH. As shown, the needle-shaped boehmite particulate material loses crystalline (as opposed to adsorbed or absorbed) water at lower temperatures and continues losing water at temperatures above ATH, extending into the 500°C range. The dynamics associated with water loss associated with the seeded boehmite particulate material may also partially explain the flame retardancy characteristics reported herein.

[0052] While the foregoing has focused on polymer composite components, such as structural components, it is also noted that the polymer composite may also be in the form of a surface coating solution, such as a polymer-containing paint formulation. Of course, like the polymer component described above, the flame retardancy characteristics are generally associated with the cured material. Accordingly, in the case of surface coating solutions, flame retardancy is associated with the cured, dried coating. For additional details of surface coating solutions, the reader is directed to

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co-pending U.S. Patent Application 10/823,400, filed April 13, 2004, Attorney Docket Number 1055-A4363, incorporated herein by reference.

[0053] According to a further aspect of the invention, the flame retardant filler may also be in the form of a blend of flame retardant components, including iron oxide, and a vitrifying component, such as metal borates, preferably zinc borate, along with the seeded boehmite particulate material described in detail above. Conventional ATH may also be incorporated. Other filler may include materials such as glass fibers, nano-clays, alumina (e.g., submicron alpha alumina), and carbon.

[0054] The polymer composite may further include thermally conductive fillers, such as alumina and boron nitride. As a result, the composite may have a thermal conductivity not less than about 0.5 W/m·K, such as not less than 1.0 W/m·K or not less than 2.0 W/m·K, particularly suitable for applications requiring a thermal transfer performance, such as a thermal interface material used in microelectronic applications.

[0055] While the invention has been illustrated and described in the context of specific embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the scope of the present invention. For example, additional or equivalent substitutes can be provided and additional or equivalent production steps can be employed. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the scope of the invention as defined by the following claims.

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WHAT IS CLAIMED IS:

1. A flame retardant polymer composite, comprising:
a polymer base material; and
a flame retardant filler provided in the polymer base material, the flame retardant filler comprising seeded boehmite particulate material having an aspect ratio of not less than 3:1.
2. The composite of claim 1, wherein the composite has a flame retardancy of V-0 or V-1 according to UL94
3. The composite of claim 2, wherein the composite has a flame retardancy of V-0.
4. The composite of claim 2, wherein the composite has said flame retardancy in cured form.
5. The composite of claim 4, wherein the composite is a polymer component.
6. The composite of claim 4, wherein the composite is in the form of a surface coating solution, the composite having said flame retardancy in coated form.
7. The composite of claim 1, wherein the polymer base material has a flame retardancy of V-2 or higher, the filler functioning to improve the flame retardancy to composite to V-1 or V-0 according to UL 94.
8. The composite of claim 1, wherein the polymer base material is selected from the group consisting of polyolefins, polyesters, fluoropolymers, polyamides, polyimides, polycarbonates, polymers containing styrene, epoxy resins, polyurethane, polyphenol, silicone, and combinations thereof.
9. The composite of claim 8, wherein the polymer base material is a non-chlorinated polymer and is a non-fluorinated polymer, and is selected from the group consisting of polyolefins, polyesters, polyamides, polyimides, polycarbonates,

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polymers containing styrene, epoxy resins, polyurethane, polyphenol, and combinations thereof.

10. The composite of claim 1, wherein the flame retardant filler further includes additional components.

11. The composite of claim 10, wherein the additional components are selected from the group consisting of iron oxide and a vitrifying agent.

12. The composite of claim 11, wherein the vitrifying agent includes zinc borate.

13. The composite of claim 1, further comprising a thermally conductive filler.

14. The composite of claim 13, wherein the thermally conductive filler is selected from the group consisting of boron nitride and alumina.

15. The composite of claim 1, wherein the composite comprises about 0.5 to 50.0 wt% flame retardant filler.

16. The composite of claim 15, wherein the composite comprises about 2.0 to 30.0 wt% flame retardant filler.

17. The composite of claim 16, wherein the composite comprises about 2.0 to 15.0 wt% flame retardant filler.

18. The composite of claim 1, wherein the seeded boehmite particulate material has an aspect ratio of not less than 4:1.

19. The composite of claim 1, wherein the seeded boehmite particulate material has an aspect ratio of not less than 6:1.

20. The composite of claim 1, wherein the seeded boehmite particulate material has an aspect ratio of not less than 9:1.

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21. The composite of claim 1, wherein the seeded boehmite particulate material predominantly comprises platelet-shaped particles, having a secondary aspect ratio of not less than 3:1.

22. The composite of claim 21, wherein the secondary aspect ratio is not less than 6:1.

23. The composite of claim 22, wherein the secondary aspect ratio is not less than 10:1.

24. The composite of claim 1, wherein the seeded boehmite particulate material predominantly comprises needle-shaped particles.

25. The composite of claim 24, wherein the needle-shaped particles have a secondary aspect ratio of not greater than 3:1.

26. The composite of claim 25, wherein the secondary aspect ratio is not greater than 2:1.

27. The composite of claim 1, wherein the average particle size of the seeded boehmite particulate material is not greater than 1000 nm.

28. The composite of claim 27, wherein the average particle size is between about 100 and 1000nm.

29. The composite of claim 29, wherein the average particle size is not greater than 800 nm.

30. The composite of claim 29, wherein the average particle size is not greater than 600 nm.

31. The composite of claim 30, wherein the average particle size is not greater than 500 nm.

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32. The composite of claim 31, wherein the average particle size is not greater than 400 nm.

33. The composite of claim 32, wherein the average particle size is not greater than 300 nm.

34. The composite of claim 1, wherein the boehmite particulate material has a specific surface area of not less than about 10 m²/g.

35. The composite of claim 34, wherein the specific surface area is not less than about 50 m²/g.

36. The composite of claim 35, wherein the specific surface area is not less than about 70 m²/g.

37. The composite of claim 36, wherein the specific surface area is not greater than about 400 m²/g.

38. A method of forming a flame retardant polymer composite, comprising:
providing a polymer base material; and
combining a flame retardant filler with the polymer base material to form the
flame retardant polymer composite, the flame retardant filler
comprising seeded boehmite particulate material having an aspect ratio
of not less than 3:1.

39. The method of claim 38, further including shape forming following combining, the flame retardant composite being a polymer component.

40. The method of claim 38, wherein the flame retardant composite is a surface coating solution.

41. The method of claim 38, wherein the composite has a flame retardancy of V-0 or V-1 according to UL94.

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42. The method of claim 41, wherein the composite has a flame retardancy of V-0.

43. The method of claim 38, wherein the polymer base material has a flame retardancy of V-2 or higher, the filler functioning to improve the flame retardancy to composite to V-1 or V-0 according to UL 94.

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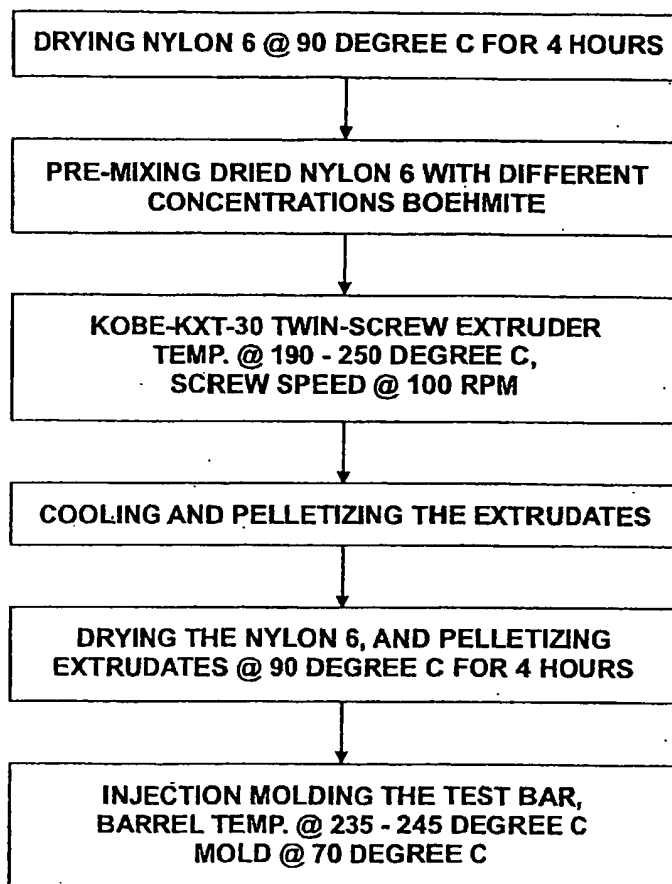


FIG. 1

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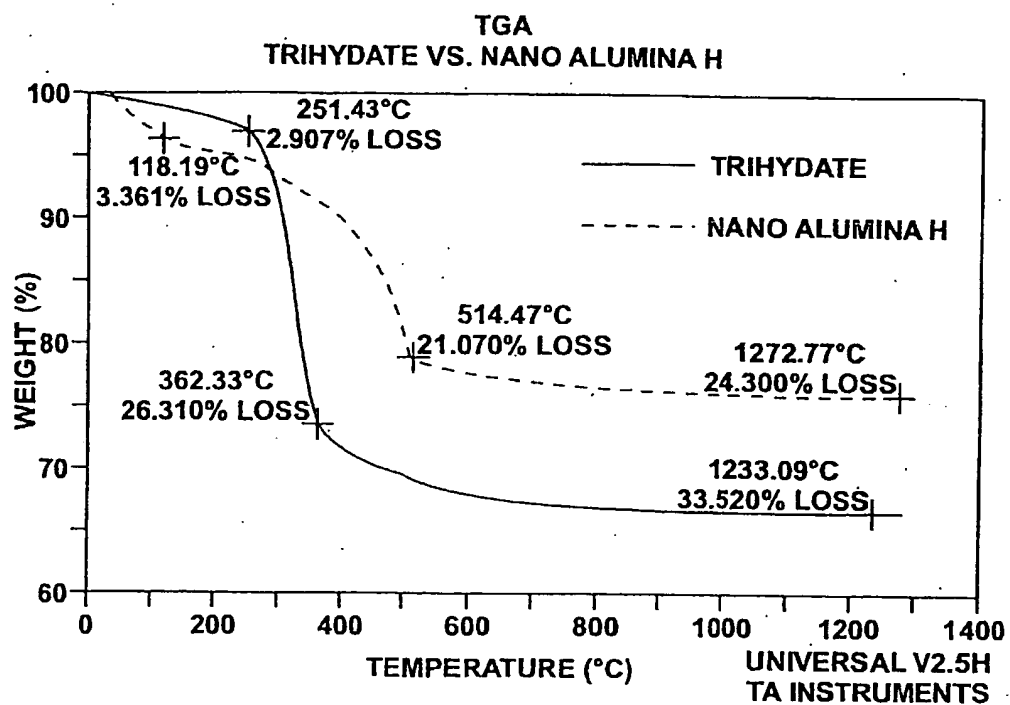


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2005/037410

A. CLASSIFICATION OF SUBJECT MATTER
C08K3/22 C08K7/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | US 2004/166324 A1 (MISHIMA HIROYUKI ET AL) 26 August 2004 (2004-08-26) page 1, paragraph 13-15 page 2, paragraphs 24,26 page 3, paragraphs 34,37 page 4, paragraph 40-42 | 1,8-20, 24-39 |
| Y | US 2003/197300 A1 (TANG HUI ET AL) 23 October 2003 (2003-10-23) page 1, paragraphs 8-12,21 page 2, paragraph 27 examples 1,2 | 1,8-20, 24-39 |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

14 March 2006

Date of mailing of the international search report

20/03/2006

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2005/037410

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| US 2004166324 A1 | 26-08-2004 | DE 10333250 A1 JP 2004059643 A TW 228388 B | 05-02-2004 26-02-2004 21-02-2005 |
| US 2003197300 A1 | 23-10-2003 | NONE | |

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